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ARTICLE *in* THE JOURNAL OF CHEMICAL PHYSICS · AUGUST 2000

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The dissociative recombination of hydrocarbon ions. III. Methyl-substituted benzene ring compounds

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(Received 21 January 2000; accepted 23 May 2000)

The recombination of electrons with cyclic ions produced via ion–molecule reactions between atomic precursor ions and methyl-substituted benzene ring compounds (toluene, ortho-, and para-xylene and mesitylene) has been studied at 300 K using a flowing afterglow Langmuir probe-mass spectrometer apparatus. Differing amounts of energy can be deposited into the daughter ions depending upon which atomic precursor is used. It has been found that same-mass daughter ions formed from different precursors displayed different recombination rate coefficients indicating that different isomeric forms were reacting. In particular, the benzene ring of the toluene cation expands to a seven-membered ring following isomerization to the cycloheptatriene form. H atom abstraction allows two different isomeric daughter ions to be formed that do not interconvert and that display different recombination rates. A similar behavior was observed for the xylenes and for mesitylene. All recombination rates lie in the range from 10^{-7} to $10^{-6}\,\mathrm{cm^3\,s^{-1}}$ and display no apparent relation with size nor with the aromaticity of the ions. © *2000 American Institute of Physics.* [S0021-9606(00)01432-X]

I. INTRODUCTION

In our systematic study of hydrocarbon ion recombination, we have measured the recombination rate of electrons with carbocations formed from linear alkanes, and with cyclic species formed from acetylene.[1,2] This paper describes a series of measurements that have been made, using the flowing afterglow Langmuir probe-mass spectrometer (FALP-MS) technique, of the recombination of ions formed from the methyl substituted benzene ring compounds: methyl-benzene (toluene), 1,2 dimethyl benzene (ortho-xylene), 1,4 dimethyl benzene (para-xylene), and 1,3,5 trimethyl benzene (mesitylene). Knowledge of these processes is important for the modeling of plasma assisted combustion processes[3] and processes involving the remediation of hydrocarbon waste streams using electrical discharge methods.[4]

This study has been made possible by the capabilities of the FALP-MS method, which allow recombination rate coefficients to be determined for individual ions even though they are part of a mixed ion plasma. The very large number of different ions formed from these parents made it necessary, however, to modify the data acquisition protocol.

II. EXPERIMENT

The flowing afterglow Langmuir probe-mass spectrometer (FALP-MS) apparatus (Fig. 1) has been described in detail elsewhere[5] and so only a brief review of the measurement method will be presented here. The technique involves an extension to the classical FALP method,[6] that includes a moveable mass spectrometer which is used to identify the ions and to measure their relative densities as a function of distance along the flow. This measurement, combined with that of the electron density, allows one to study the recombination of one particular ion, even if other ions, also present in the flow, undergo recombination. The pollution of surfaces at room temperature by the neutral parents necessitated the use of a heated Langmuir probe, which is described in detail elsewhere.[7]

A. Precursor ions

In the apparatus, an afterglow was formed in a helium buffer gas, introduced at a rate of 24 sl min, into a cylindrical glass tube surrounded by a microwave cavity operating at 2.45 GHz. This afterglow contained neutral ground state and metastable excited state helium atoms, He^+ and He_2^+ ions.

The measurements reported here were performed at a pressure of 0.5 Torr corresponding to a helium density of $1.6\times10^{16}\,\mathrm{cm^{-3}}$. Under these conditions, the flow velocity was 22 000 cm/s (corresponding to a hydrodynamic measuring time of 0.5 ms), and the initial electron density was varied from 10^9 to $10^{10}\,\mathrm{cm^{-3}}$. Three precursor gases, Xe, Kr, or N_2 were used to form the ions to be studied, and were introduced at a second entry port, downstream of the microwave cavity, so as to produce a plasma dominated by Xe^+, Kr^+, or N^+/N_2^+ via the reactions[8,9]

$$He^+ + 2He \xrightarrow{k_1} He_2^+ + He \quad k_1 = 8.3\times10^{-32}\,\mathrm{cm^6\,s^{-1}},$$

and

$$He^+ + Xe(\text{or } Kr) \xrightarrow{k_2} He + Xe^+(\text{or } Kr^+)$$

$$k_{2,Kr} < 10^{-11}\,\mathrm{cm^3\,s^{-1}},$$

$$k_{2,Xe} = 8\pm1\times10^{-12}\,\mathrm{cm^3\,s^{-1}},$$

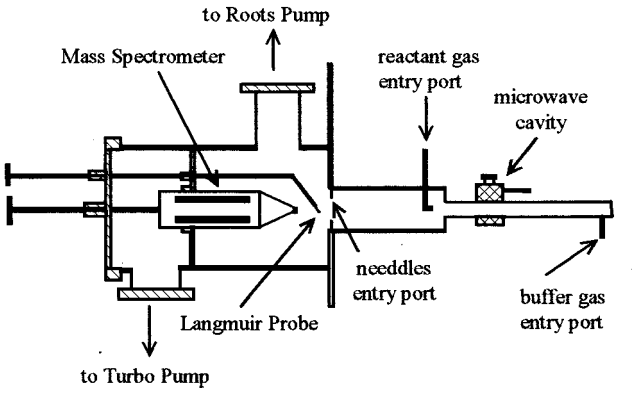

FIG. 1. The FALP-MS apparatus.

$$He_2^+ + Xe(\text{or } Kr) \xrightarrow{k_3} 2He + Xe^+(\text{or } Kr^+)$$

$$k_{3,Kr} = 1.85 \times 10^{-11}\ cm^3\ s^{-1},$$

or

$$He^+ + N_2 \xrightarrow{k_4} He + N_2^+ \quad (44\%) \quad k_4 = 1.5 \times 10^{-9} cm^3\ s^{-1},$$

$$\xrightarrow{k_4} He + N^+ + N(56\%),$$

$$He_2^+ + N_2 \xrightarrow{k_5} 2He + N_2^+ \quad k_5 = 1.3 \times 10^{-9}\ cm^3\ s^{-1}.$$

The metastable helium atoms $He^M(2\,^3S)$ are destroyed by Penning ionization[10,11]

$$He^M + Kr \xrightarrow{k_6} Kr^+ + e + He \quad k_6 = 1.0 \times 10^{-10}\ cm^3\ s^{-1},$$

$$He^M + Xe \xrightarrow{k_7} Xe^+ + e + He \quad k_7 = 1.2 \times 10^{-10}\ cm^3\ s^{-1},$$

$$He^M + N_2 \xrightarrow{k_8} N_2^+ + e + He \quad k_8 = 8 \times 10^{-11}\ cm^3\ s^{-1},$$

and N_2^+ is removed by dissociative recombination ($\alpha = 2.6 \times 10^{-7}\ cm^3\ s^{-1}$).[12]

The parent vapors of the ions to be studied were introduced through the needle entry port, located further downstream as shown in the figure. At this point, mass spectrometric measurements indicated that the plasma contained no He^+ or He_2^+, (and so one could be sure that all helium metastables, He^M were destroyed), and consisted of either Kr^+ or Xe^+ or of a mixture of N^+ and N_2^+.

B. Measurement of the recombination rate coefficient

M^+, the ion whose recombination is studied, is produced via an ion–molecule reaction between its neutral parent and the precursor ion (N^+, Kr^+, or Xe^+). Its density in the flow may be diminished through recombination with electrons (with a rate coefficient, α), by reactions with a neutral N (with rate, k), N being either an impurity or the neutral parent of M^+, and via diffusion (with ambipolar diffusion coefficient, D_A). The equation of the decay of $[M^+]$ vs. distance z along the flow (velocity of the flow v) is given by

$$\frac{d[M^+]}{dt} = v\frac{d[M^+]}{dz}$$

$$= -\alpha[M^+][e] - k[M^+][N] - \frac{D_A}{\Lambda^2}[M^+],$$

where Λ is the characteristic diffusion length, and longitudinal diffusion is neglected. This equation can be integrated from an arbitrary initial point z_0 to the point z downstream where the measurement is made, yielding

$$v \ln\frac{[M^+]}{[M^+]_{z_0}} = -\alpha\int_{z_0}^{z}[e]dz - \left(k[N] + \frac{D_A}{\Lambda^2}\right)(z - z_0).$$

It should be noted that this mathematical analysis assumes that no source of M^+ remains in the recombination zone, and that the neutral parent does not attach electrons.

It can be seen from this last equation that a plot of $\ln[M^+]_z/[M^+]_{z_0}$ vs. $1/v\int_{z_0}^{z}[e]dz$ will yield α. This plot can be made by measuring the electron and ion densities at several points along the axis, this method being called the ''variable z'' method. If reactions with neutrals and diffusion are not negligible, this plot will give an upper limit for the recombination rate. Since the terms representing losses other than reaction with electrons are independent of electron density, plotting $\ln[M^+]_{z_1}/[M^+]_{z_0}$ vs. $1/v\int_{z_0}^{z_1}[e]dz$ at fixed position z_1 for different initial electron densities, yields the rate coefficient even if these effects are not negligible. This method is referred to as the ''fixed z'' method. It has to be said however, that when $[M^+]$ represents several isomers reacting at different rates, a curvature is seen in the $\ln[M^+]_z/[M^+]_{z_0}$ vs. $1/v\int_{z_0}^{z}[e]dz$ plot (''variable z''), and the ''fixed z'' data treatment is no longer valid. In such cases, only the upper limit provided by the ''variable z'' method is available.

Measurement of the flow velocity is necessary in order to evaluate the rate coefficient and this is performed by modulating the discharge and by measuring the time-of-flight of the ionization pulse along the flow, using a Langmuir probe. This measurement represents the major source of error in the rate coefficient determination and the results presented in this article are estimated to be accurate to $\pm 30\%$. Measurement of the density of M^+ along the flow is performed using a moveable mass spectrometer. The ions formed in this experiment can react with their neutral parents to form dimer ions, thus leading to masses up to 250 that must be taken into consideration to determine the density of the ion under study. To minimize mass discrimination effects, the whole spectrum is recorded with the lowest resolution (Fig. 2). Often, not only M^+ is formed, but also $(M-1)^+$ and sometimes $(M+1)^+$, and a higher resolution is required in order to separate the different masses. For these cases, the portion of interest of the mass spectrum is recorded again at high resolution (Fig. 3), so as to determine the relative intensities of the different masses, leading finally to the measurement of $[M^+]$.

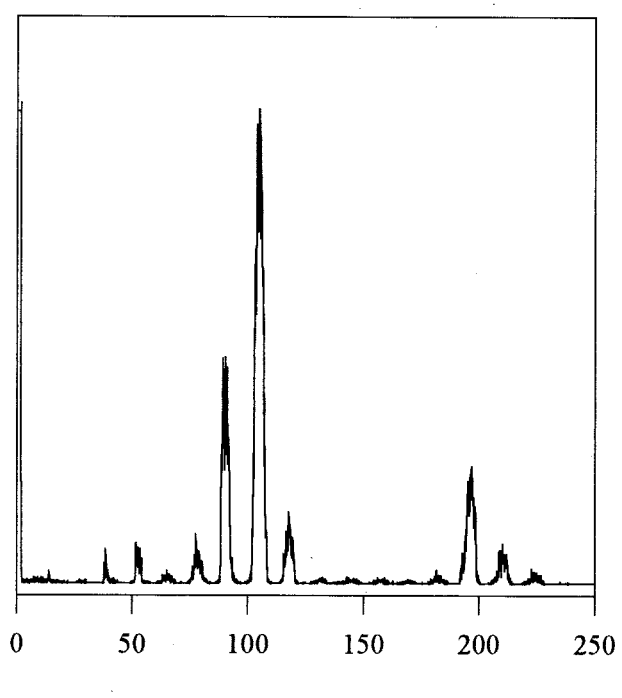

FIG. 2. Mass spectrum at low resolution in the 0–250 mass range, ions resulting from $N^+ + p$-xylene.

III. FORMATION OF THE IONS

A. Injection of the vapors

The hydrocarbons used in this experiment were obtained from Aldrich, and had a purity greater than 99% and thus were used without further purification. The hydrocarbon vapors were injected into the apparatus by passing a helium flow $q(\mathrm{He})$ through the hydrocarbon liquid, contained in a ''bubbler vessel.'' The total pressure in the bubbler, P_{bubbler} was maintained low enough so as to ensure a sufficiently high hydrocarbon/helium mixing ratio in the afterglow apparatus, to remove the precursor ion from the flow. The bubbler and its content were cooled to below room temperature, in order to avoid condensation in the injection line.

The flow rate q of parent hydrocarbon can be calculated using the equation

$$q(\mathrm{parent}) = q(\mathrm{He}) \times \frac{P_{\mathrm{Parent}}}{P_{\mathrm{bubbler}} - P_{\mathrm{Parent}}},$$

where P_{Parent} is the vapor pressure of the hydrocarbon at the temperature of the bubbler. This device allowed the hydrocarbon flow rate to be maintained constant, and the maximum hydrocarbon densities used ranged from $4 \times 10^{13}\,\mathrm{cm}^{-3}$ (toluene) to $10^{13}\,\mathrm{cm}^{-3}$ (mesitylene).

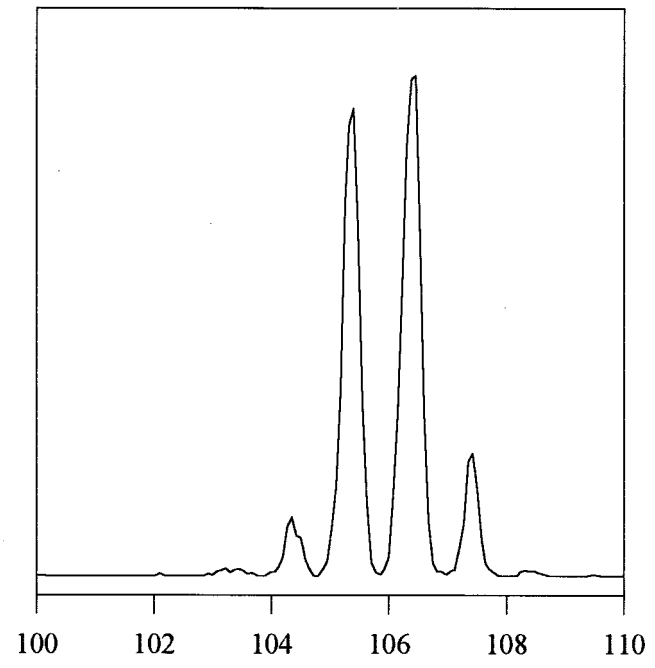

FIG. 3. Detail of Fig. 2: high resolution scan in the 100–110 mass range.

B. Ions formed from toluene injection

The first step in the formation of the ions to be studied, is the charge-exchange reaction with the precursor ion, which forms toluene cations $C_7H_8^+$. The energetics of the reaction are thus that these cations can be formed with as much as 6.75 eV of internal energy, meaning that they can be electronically excited or even can undergo dissociation. In their study of the unimolecular decay of toluene ions, Bombach *et al.*[13] have stated that the excess electronic energy is rapidly converted ($t < 1\ \mu$s) into vibrational energy of the electronic ground state, and such vibrationally excited states are also efficiently relaxed by resonant charge-exchange reaction with neutral toluene. We have limited our measurements of dissociative recombination rates to the ions $C_7H_8^+$ (92^+) and $C_7H_7^+$ (91^+), although the product resulting from $-CH_3$ loss was also observed in addition to smaller dissociation products.

The dissociation of toluene cations, and particularly the formation of $C_7H_7^+$ ions, has been studied for more than 40 years, from a thermodynamic and kinetic point of view (Ref. 14, and references therein). The positive ions of interest formed from toluene include toluene $TOL^{\bullet +}$ (92^+), cycloheptatriene $CHT^{\bullet +}$ (92^+), benzylium Bz^+ (91^+), and tropylium ions Tr^+ (91^+) depending on the amount of energy deposited into the toluene by the precursor ion. These four ions are linked together via the reaction scheme of Fig. 4.[13–15]

$TOL^{\bullet +}/CHT^{\bullet +}$ interconversion and H- abstraction have been studied using *ab initio* theory,[16] and the main features of the resulting potential energy surface are represented in Fig. 5. The shape of this surface has important consequences for the nature of the ions formed in our experiment. First, there is no energy range where pure Tr^+ is produced, as the appearance energies of Tr^+ and Bz^+ from $TOL^{\bullet +}$ are almost identical (2.17 and 2.13 eV, respectively). Second, the isomerization barrier from $TOL^{\bullet +}$ to $CHT^{\bullet +}$ is 1.96 eV, and the reverse barrier is 1.21 eV. Thus when mass 92^+ dissociates, isomerization occurs and $TOL^{\bullet +}$ and $CHT^{\bullet +}$ are pro-

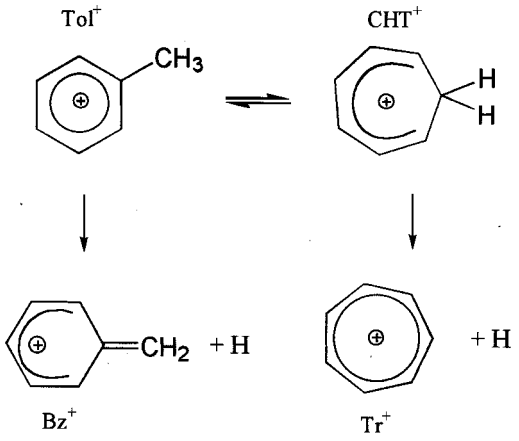

FIG. 4. Reactions linking the toluene and cyclohetatriene ions with the benzylium and tropylium ions.

duced. Conversely, when the energy deposited in $TOL^{\bullet+}$ is sufficiently low so as to avoid dissociation, isomerization should also be avoided.[15]

C. Ions formed from xylenes and mesitylene injection

The number of daughter ions increases with the size of the neutral parent. The ions whose dissociative recombination rates have been measured are the daughter ions that have resulted from pure charge exchange, H- abstraction and $-CH_3$ abstraction reactions. This choice is guided by the lack of data concerning the formation of the other ions. The ions studied in this experiment must be terminal ions, and their parents must have been destroyed prior to the dissociative recombination rate measurement. As a consequence, we have restricted our measurements to ions that are formed by a single bond break or by direct charge exchange. An ion cyclotron resonance ion–molecule study[17] of the reactivity of one of the daughter ions from *p*-xylene or *o*-xylene (namely the benzyl ion), with *p*-xylene indicated that one of the products is 105^+, the other being 119^+. With *o*-xylene, the only product is 119^+. This explains why we do not report measurements of the dissociative recombination of ion 105^+ formed from *p*-xylene. For the other parents, the validity of this choice has been checked by a study of the ions' abundances as a function of the neutral parent injection rate, that indicates that the charge-exchange products dissociate on a time scale that is small compared to our hydrodynamic time (the time for the ions to move along the flow from their point of production to their point of detection), and that the chosen ions are actually suitable for recombination measurements.

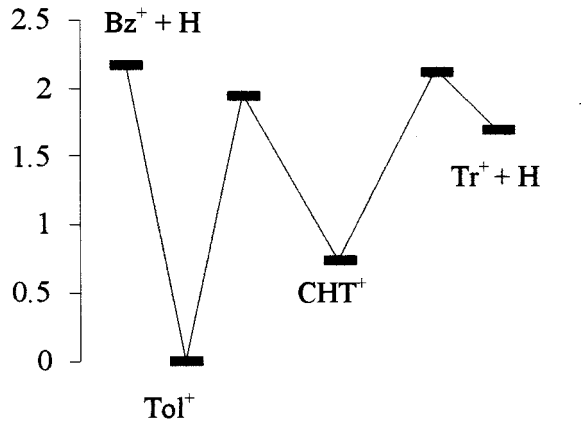

FIG. 5. Schematic potential energy diagram (relative energies in eV).

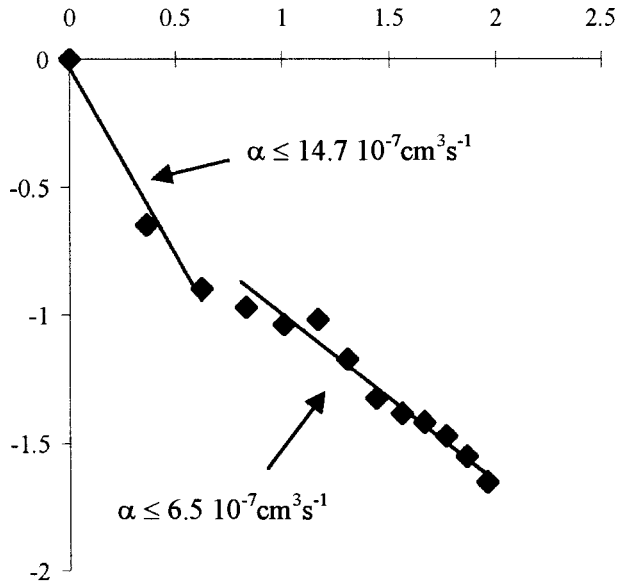

FIG. 6. Logarithmic decay of the density of 91^+ vs. the integral of electron density, ions produced from N^++toluene.

IV. RESULTS

When several isomers reacting at different recombination rates coexist, the ''fixed *z*'' method cannot be used. This is the case for 91^+ and 105^+, for which the plots of $\ln[M^+]_z/[M^+]_{z_0}$ vs. $1/v\int_{z_0}^{z}[e]dz$ exhibit a marked curvature (Figs. 6 and 7). It should also be kept in mind that the use of this method requires that the initial electron density be varied over an appreciable range, yet kept sufficiently high so as to be measured with the Langmuir probe. In the case of 119^+ and 120^+, formed from mesitylene with N^+ as precursor, we were unable to achieve such a variation, as our highest initial electron density was too low, so only an upper value has been measured using the variable *z* method. The isomer assignment will be discussed in the next section.

V. DISCUSSION

A. Ions formed from direct charge transfer: 92^+, 106^+ and 120^+

The two values found for the recombination of 92^+ formed from N^+ and from Xe^+ are very different and cannot be explained in terms of experimental uncertainties. The reason for this must be due to differences in the structures of the ions studied. In fact the excess energy deposited into the 92^+ ions following the charge exchange reaction with the precursor ion varies from 6.75 eV for N_2^+ to 3.30 eV for Xe^+,[18] and

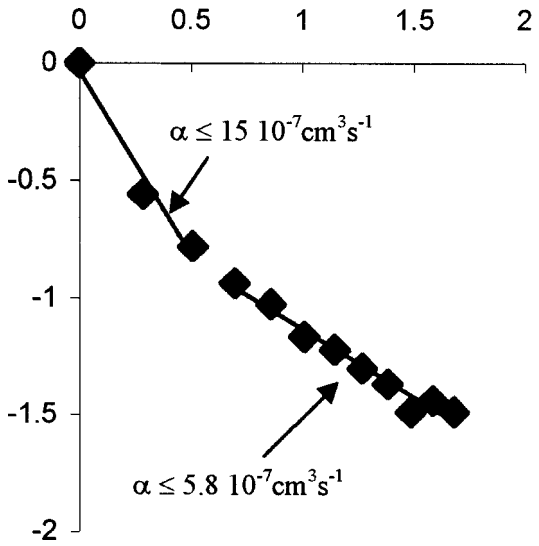

FIG. 7. Logarithmic decay of the density of 105^+ vs the integral of electron density, ions produced from $N^+ + o$-xylene.

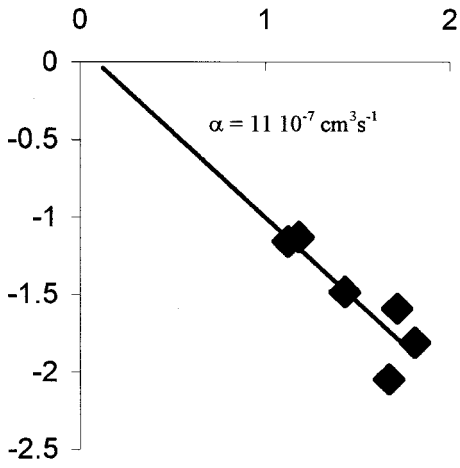

FIG. 9. Logarithmic decay of the density of 92^+ vs the integral of electron density, ''fixed z'' method, $z = 90$ mm.

one can see from the mass spectra that while 92^+, formed from N^+, dissociates, this does not occur if the precursor is Xe^+. This dissociation energy is however, very close to the activation energy for the rearrangement of $TOL^{\bullet +}$ into $CHT^{\bullet +}$, and one can surmise therefore, that in the case of the formation via Xe^+, the cation will have the same structure as its parent and the ion studied is $TOL^{\bullet +}$. Ions formed from N^+ will therefore be a mixture of $TOL^{\bullet +}$ and $CHT^{\bullet +}$. Thus the measured value for the recombination coefficient will be a mean of the coefficients for $TOL^{\bullet +}$ and $CHT^{\bullet +}$. In this case, the value for the recombination of $CHT^{\bullet +}$ must be greater than that for $TOL^{\bullet +}$, and the fact that no curvature is seen in Figs. 8 and 9 reflects either the rapid interconversion between $TOL^{\bullet +}$ and $CHT^{\bullet +}$ or that CHT^+ is produced in a far greater amount than $TOL^{\bullet +}$.

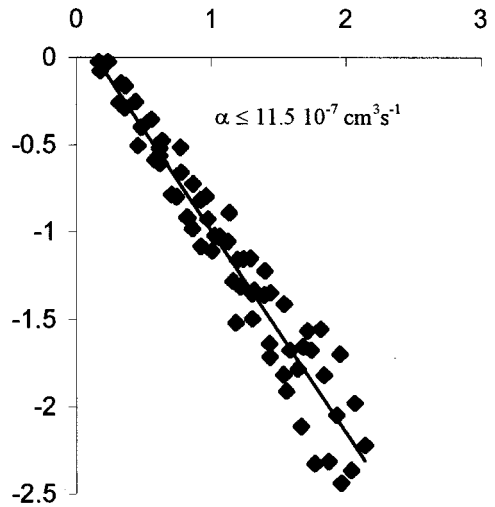

FIG. 8. Logarithmic decay of the density of 92^+ vs. the integral of electron density, ''variable z'' method.

To our knowledge, no similar study has been made concerning the potential energy surfaces for ions 106^+ or 120^+. The similarity however, between the behavior seen for 91^+ and 105^+ makes one think that perhaps similar mechanisms are in play and that an expansion of the six-member benzene ring toward a seven-member ring occurs. The values measured for 120^+ formed from N^+ and from Xe^+ are however, difficult to compare, one being an upper value.

B. Other ions: 91^+, 105^+, 119^+

1. 91^+

The 91^+ ions are formed by H-abstraction from 92^+ or CH_3-abstraction from 106^+. The curvature seen in the graph of $\ln[M^+]_z/[M^+]_{z_0}$ vs. $1/v\int_{z_0}^{z}[e]dz$ for the 91^+ ion, produced from toluene (Fig. 6) is also observed for 91^+ ions produced from 106^+. This curvature can be explained by the presence of two isomers Bz^+ and Tr^+ which recombine at different rates. Along with the prediction based upon the potential energy surface for the simultaneous formation of two ions,[14] the presence of Bz^+ is confirmed by the formation, in a plasma formed from toluene injection, of an ion of mass 105 via the reaction

$$Bz^+ + \text{toluene} \rightarrow C_8H_9^+ + \text{fragments},$$

which is relatively rapid ($k \geqslant 1.6\times10^{-10}\,\text{cm}^3\,\text{s}^{-1}$) and is often used in the titration of Bz^+ ions.[19–21] This method has demonstrated in other studies that the ratio Tr^+/Bz^+ strongly depends upon the excess energy deposited into the toluene molecule by the precursor ion.[15,19] Tr^+ is apparently rather unreactive and no other ion–molecule reaction concerning this ion is found in the literature. Although exothermic, the rearrangement of Bz^+ by collisions to Tr^+ has not been reported, in either the gaseous or the condensed phase,[15,19] but is observed in argon matrixes when photochemically induced.[22] On the other hand, Bz^+ reacts with numerous molecules and in particular with toluene yielding the adduct with mass 183^+, thus,

$$Bz^+ + \text{toluene} \rightarrow C_7H_7.C_6H_5CH_3^+ \quad k = 2\times10^{-9}\,\text{cm}^3\,\text{s}^{-1}.$$

TABLE I. Recombination rates (in $cm^3\,s^{-1}$) of the ions whose mass appears in column 1. The isomer assignment is discussed in the text.

Ion	Parent	Precursor ion	Isomer assignment	Recombination rate	Method
91^+	Toluene, xylenes	N^+	benzylium	<10	variable *z*
	Toluene, xylenes	N^+	tropylium	3.2	fixed *z*
92^+	Toluene	N^+	$TOL^+ + CHT^+$	11	fixed *z*
		Xe^+	TOL^+	6	fixed *z*
105^+	*o*-xylene, mesitylene	N^+	xylyl cation	<12	variable *z*
		N^+	methyl-tropylium	<5	variable *z*
		Kr^+	methyl-tropylium	5.7	fixed *z*
106^+	*o*-xylene, *p*-xylene	N^+		5.7–7.3	fixed *z*
119^+	Mesitylene	N^+	Mesitylyl cation	<9	variable *z*
			dimethyl-tropylium	not measurable	variable *z*
120^+	Mesitylene	N^+		<10	variable *z*
		Xe^+		6.4	fixed *z*

This reaction has been used in a study of 91^+ ions produced from toluene, where we could achieve a sufficiently high toluene flow rate to ensure the conversion of the Bz^+ ions into the adduct, leaving Tr^+ as the only form representative of 91^+. The curvature that was observed with lower rates then disappeared and the similarity between the measured recombination rates for the remaining 91^+ ion measured using variable *z* and fixed *z* methods, confirmed that Tr^+ is actually nonreactive with toluene via ion–molecule reactions.

2. 105^+ and 119^+

While at least 13 long-lived isomers have been found for the 105^+ ion in a collisional activation mass spectrometry experiment,[23] no complete study of their relative stability has been performed. In our experiment, judging by their calculated[24] or measured[25] heats of formation, at least three of them can be formed from *o*-xylene. These are the *o*-methylbenzyl, methyl-tropylium, and homotropylium cations. The latter has been the object of more detailed structural analyses, being a prototype of a homo-aromatic system.[26,27] Its formation requires the expansion of the benzene ring out to an eight-membered ring, and this ring expansion is considered to be a relatively slow rearrangement.[13] As tropylium ions are formed prior to recombination with electrons, however, the formation of homotropylium cations can not be excluded.

To our knowledge, nothing is known concerning the ion–molecule reactivity of the different isomers. It is likely that the methylbenzyl ions will behave similarly to the benzyl cation, and the methyl-tropylium, like the tropylium. In this case, the association product observed at mass 211 has been formed from methylbenzyl ions. Unfortunately, we were not able to maintain a suitable electron density while injecting an amount of *o*-xylene sufficient to eliminate all the methylbenzyl cations by ion–molecule reaction. All our measurements therefore show the curvature related to the presence of at least two different isomers, the ion which recombines the most rapidly being, by analogy with our measurements with 91^+, methylbenzyl, the slowest recombination being attributed to other isomeric forms, among them the methyl-tropylium ion.

The situation is even more complex for the ions formed from mesitylene, on one hand due to the total lack of information concerning the different ions and on the other due to the technical difficulties associated with handling the large number of ions formed in the flow. It is also the case that curvature is found for the decrease of the density of the ion 119^+ and by analogy the fastest recombination rate is attributed to the trimethyl-benzyl ion. The recombination rate for the other 119^+ ions could not be measured due to the too small electron density and the scattering of the data points.

VI. CONCLUSION

As has already been noted in our study of saturated and nonsaturated hydrocarbon ions, no relation seems to exist between the size of the ion and its recombination rate with electrons. The present study shows that the reactivity with electrons has no relation with the aromaticity of the ion. Reindl *et al.*[24] have evaluated the aromatic character of delocalized cyclic ions and have confirmed the high aromaticity of tropylium, while that of benzylium is strongly reduced compared to benzene. In fact, they suggest that the best description of the benzylium ion is the quinoid structure (see Fig. 4). The recombination rate for the benzene cation $C_6H_6^+$ ($10^{-6}\,cm^3\,s^{-1}$) however, is similar to that for benzylium, while that for tropylium is $3.2\times10^{-7}\,cm^3\,s^{-1}$.

The large number of ions formed from toluene, the xylenes, and from mesitylene has made the determination of rate coefficients very difficult in this experiment. The measured coefficients presented here, and summarized in Table I, should, therefore, be treated more as orders-of-magnitude rather than as exact values. The study of the decrease of $1/n_e$ as a function of distance *z* however, yields a global rate coefficient for the ensemble of ions present in the flow and since this always seems to yield a value of several times $10^{-7}\,cm^3\,s^{-1}$, it indicates that none of the ions seem to have extremely large rate coefficients (as is the case, for example for some cluster ions). This global decrease also exhibits the curvature observed for odd numbered masses, indicating that it is not an experimental artifact. It is evident that the presence of the neutral parent molecule in the flow represents a serious drawback for these recombination measurements since the initial ions react with it producing other species.

One cannot select *a priori* the ion that one wants to study. It would be extremely interesting to be able to inject individual ions directly into the plasma, even without mass preselection. The development of such a system is currently underway.

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